United States
Department of
Agriculture

Food Safety
and Inspection
Service

Science and
Technology

Chemistry
Division

August 1993

Symposium On New And Emerging Approaches To The Development of Methods In Trace-Level Analytical Chemistry

HAZARDOUS WASTE REDUCTION IN THE DEVELOPMENT OF ANALYTICAL METHODS - SUPERCRITICAL FLUID EXTRACTION

Jerry W. King
Food Quality & Safety Research Unit
National Center for Agricultural Utilization Research
Agricultural Research Service/USDA
Peoria, IL 61604

In 1987, the Supercritical Fluid Technology Group at NCAUR initiated a research program on behalf of FSIS to explore the use of SFE and SFC for residue analysis. This research program has been very successful and has made significant contributions over the past five years to the development and utilization of SFE in analytical chemistry. A key feature of the program has been the development of techniques and methods which can be incorporated directly into a working residue analysis laboratory. This presentation will highlight those accomplishments, describe current research being undertaken at NCAUR, and suggest future research which should be undertaken to assure the integration of SFE into analytical protocols.

Efforts at NCAUR have centered on the development of methods for pesticide residues in meats, grains, and assorted food products. Early efforts focused on the quantitative removal of fat from a variety of meat products and moderating the role of water during the SFE. Currently, lipid phases can be reproducibly extracted from numerous meat products with high precision (> 1% RSD), provided samples are properly prepared prior to extraction. This development was greatly aided by the incorporation of a patented "supercritical fluid extraction enhancer" into the methodology.

Numerous discussions with FSIS field laboratories have revealed the importance of sample size for low fat meat products and the need for equipment which can process large numbers of samples. Our laboratory has addressed both these needs by developing the technology necessary to process large samples using SC-CO_2. In addition, we have developed the first multi-sample SFE system which has evolved to a third generation instrument. This unit, capable of processing 6-8 samples simultaneously, has been commercialized in a modified form by Dionex Corporation. Currently our laboratory is in the process of installing an NCAUR-built unit in FSIS's Alameda laboratory.

Commercial SFE instrumentation has also been evaluated at NCAUR to assess its applicability for regulatory analysis. Research has shown that several SFE-based residue analysis methods can be translated onto these commercial modules. However sample size and the number of samples that can be extracted on these units is compromised due to inadequate fluid delivery systems and the pressure limitations associated with this commercial equipment. Companies which produce SFE instrumentation are beginning to

address some of the above problems, however further commercial developments are impeded by a number of complex and interrelated factors, including regulatory agency acceptance of SFE methods.

Analytical SFE currently lacks extraction specificity for many applications involving the analysis of foods and must be supplemented or combined with other cleanup methodologies. The use of sorbent-based methodologies integrated into the SFE step or used after SFE appear to hold much promise. Research in our laboratory has demonstrated that a fat-free SFE extract can be obtained by selective fractionation of the pesticide moieties from the lipid coextractives. Current research employing selective sorption of target analytes on ion exchange media also appears to be promising.

Extraction of polar analytes from food matrices is not always successful using neat supercritical fluids. These results may be due to sample matrix effects as well as solute solubility limitations in supercritical fluid media. Recent research at NCAUR has shown the necessity for employing cosolvents for the extraction of polar analytes, such as aflatoxins from grain and taxol from yew wood. The need to use small quantities of organic solvents in many SFE procedures is becoming readily apparent as the technique matures.

The need to develop analytical procedures for the rapid screening of large numbers of meat samples, on-site, is of immediate concern to FSIS. Research at NCAUR has demonstrated that SFE can be combined with available immunoassay methods to allow the qualitative determination of pesticides in meat samples. Concurrent with this development, we have been investigating novel ways of conducting SFE in the field using simple, inexpensive methodology. Results to date, utilizing dry ice as an extraction medium, have yielded incomplete extraction (<50% recovery) and excessive extraction times. This has recently been improved by using cosolvents or using the phase behavior of SC-CO_2 to achieve higher analyte recoveries.

Finally, several complementary supercritical fluid-based techniques show promise in addressing FSIS's current needs. Supercritical fluid chromatography is now being reinvestigated at NCAUR for sample cleanup, both in the on-line and off-line SFE modes. Recent developments in SFC instrumentation may allow alternative methods to be developed, which will minimize the use of organic solvents used in HPLC procedures. Utilization of SC-CO_2 for the desorption of trapped compounds in the purge and trap step of a conventional headspace analysis routine, shows considerable promise in profiling off-flavor components and degradation products associated with food product spoilage.